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(54) Synergistic organomolybdenum compositions and lubricating compositions containing same

(57) This invention relates to synergistic antiwear compositions comprising an organomolybdenum complex and an organic sulfur compound selected from 2,5-dimercapto-1,3,4-thiadiazole derivatives, bisdithiocarbamate esters, metal dithiocarbamates, metal phosphorodithioates and phosphorodithioate esters. The organomolybdenum complex is a reaction product prepared by reacting 1 mole fatty oil, 1.0 to 2.5 moles diethanolamine and a molybdenum source.

Lubricating compositions containing the synergistic compositions possess good antiwear properties and improved oxidation stability.

EP 0 874 040 A1

Description

BACKGROUND OF THE INVENTION

The invention concerns lubricating compositions having improved properties. Another aspect of the invention relates to additive compositions which impart antiwear and antiscuffing properties to lubricating compositions used for internal combustion engines such as gasoline engine and diesel engine.

Additives known as antiwear agents are employed to increase the load carrying capacity of lubricants. The antiwear agents promote the formation of a surface film and thereby prevent wear of the contacting surfaces. The mechanical efficiency enhanced by decreased friction loss further results in decreased fuel consumption and energy savings.

It is known that certain organic molybdenum complexes possess antiwear properties as well as other desirable lubricating characteristics as disclosed in U.S. Pat. No. 4,889,647. Surprisingly, it has been now discovered that the molybdenum complexes described therein produce a synergistic antiwear effect in combination with certain organic sulfur compounds.

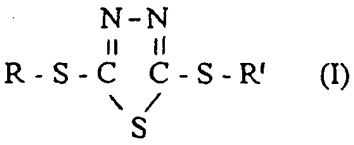
SUMMARY OF THE INVENTION

According to the invention, there are provided synergistic antiwear compositions comprising:

(1) an organomolybdenum complex prepared by reacting about 1 mole fatty oil, about 1.0 to 2.5 moles diethanolamine and a molybdenum source sufficient to yield about 0.1 to 12.0 percent of molybdenum based on the weight of the complex, and

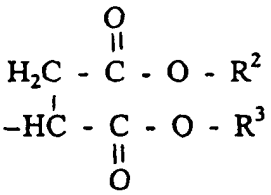
(2) an organic sulfur compound selected from the group consisting of

(i) 1,3,4-thiadiazole compounds of the formula:



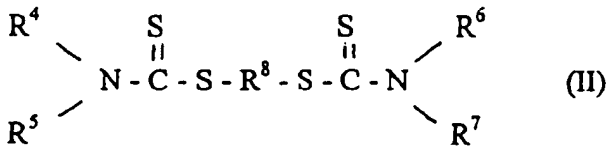
(I)

wherein R and R' are independently selected from C_{1-22}-alkyl groups, terpene residue and maleic acid residue of the formula



and R^2 and R^3 represent C_{1-22}-alkyl and C_{5-7}-cycloalkyl groups, either R^2 or R^3 may be hydrogen and either R or R' may be hydrogen when R^2 or R^3 are C_{9-22}-alkyl groups;

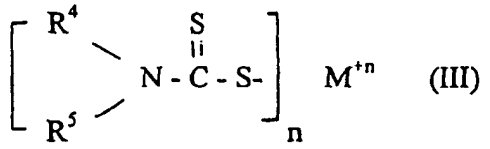
(ii) bisdithiocarbamate compounds of the formula



(II)

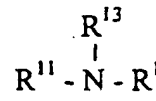
wherein R^4, R^5, R^6, and R^7 are aliphatic hydrocarbyl groups having 1 to 13 carbon atoms and R^8 is an alkylene group having 1 t 8 carbon atoms;

(iii) dithiocarbamates of the formula



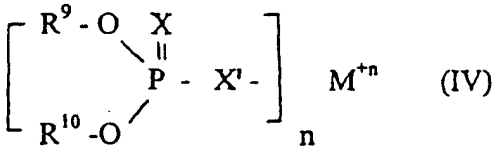
(III)

wherein R^4 and R^5 represent alkyl groups having 1 to 8 carbon atoms, M represents metals of the periodic groups IIA, IIIA, VA, VIA, IB, VIB, VIII and a salt moiety formed from an amine of the formula



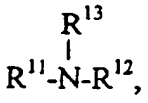
R^{11}, R^{12} and R^{13} being independently selected from hydrogen and aliphatic groups having 1 to 18 carbon atoms and n is the valence of M;

(iv) phosphorodithioates of the formula



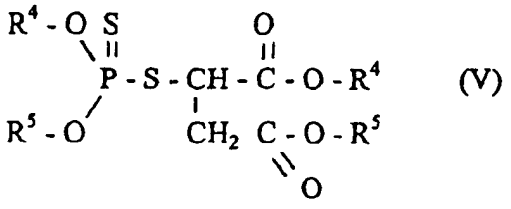
(IV)

wherein X and X' are independently selected from S and O, R^9 and R^{10} represent hydrogen and alkyl groups having 1 to 22 carbon atoms, M represents metals of the periodic groups IIA, IIIA, VA, VIA, IB, VIB, VIII and a salt moiety formed from an amine of the formula



R^{11}, R^{12} and R^{13} being independently selected from hydrogen and aliphatic groups having 1 to 18 carbon atoms and n is the valence of M; and

(v) phosphorodithioate esters of the formula



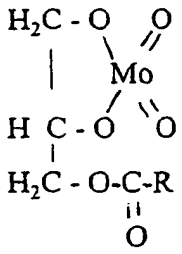
(V)

wherein R^4 and R^5 may be the same or different and are selected from alkyl groups having 1 to 8 carbon atoms; and the ratio of the molybdenum complex to the sulfur compound is about 1:5 to about 5:1.

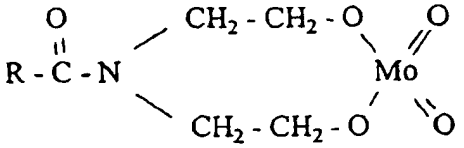
Another aspect of the invention concerns lubricating compositions having improved lubricating properties and comprising a major portion of an oil of lubricating viscosity and about 0.1 to 10.0 percent by weight of a composition comprising (1) an rganomolybdenum complex prepared by reacting about 1 mole fatty oil, about 1.0 to 2.5 moles diethanolamine and a molybdenum source sufficient to yield about 0.1 to 12.0 percent of molybdenum based on the weight of the complex and (2) a sulfur compound of the formula I, II, III, IV or V.

DETAILED DESCRIPTION OF THE INVENTION

The organomolybdenum component of the invention is prepared by sequentially reacting fatty oil, diethanolamine and a m lybdenum source by the condensation method described in U.S. Pat. No. 4,889,647, incorporated herein by reference. Th reaction yields a reaction product mixture. The major components are believed to hav the structural formulae



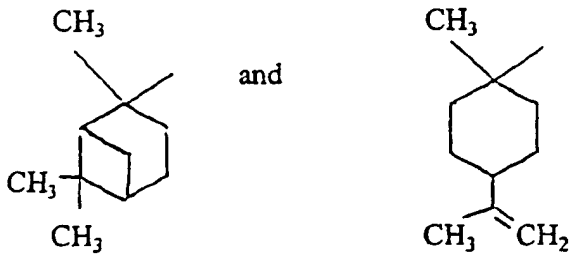
and



wherein R represents a fatty oil residue. The preferred fatty oils are glyceryl esters of higher fatty acids containing at least 12 carbon atoms and may contain 22 carbon atoms and higher. Such esters are commonly known as vegetable and animal oils. Vegetable oils particularly useful are oils derived from coconut, corn, cottonseed, linseed, peanut, soybean and sunflower seed. Similarly, animal fatty oils such as tallow may be used.

The source of molybdenum is an oxygen-containing molybdenum compound capable of reacting with the intermediate reaction product of fatty oil and diethanolamine to form an ester-type molybdenum complex. The source of molybdenum includes, among others, ammonium molybdates, molybdenum oxides and mixtures thereof.

The 1,3,4-thiadiazoles of formula I may be prepared by the method disclosed in U.S. Pat. No. 4,761,842 and U.S. Pat. No. 4,880,437. Terpene residues are preferably derived from pinene and limonene having the structural formulae given hereinbelow.



and

The alkyl groups represented by R and R' contain preferably 1 to 22 carbon atoms and may be branched or straight chain. Particularly preferred are compounds wherein both alkyl groups together contain a total of at least 22 carbon atoms. Groups R^2 and R^3 in the formula I represent branched or straight chain alkyl groups containing 1 to 22 carbon atoms and cyclic aliphatic groups such as cyclohexyl, cyclopentyl and cycloheptyl.

The bisdithiocarbamates of formula II are known compounds described in U.S. Pat. No. 4,648,985, incorporated herein by reference. The compounds are characterized by groups R^4 to R^7 which are the same or different and are hydrocarbyl groups having 1 to 13 carbon atoms. The group R^8 is an aliphatic group such as straight and branched alkylene groups containing 1 to 8 carbons. Particularly preferred is methylenebis (dibutyldithiocarbamate) available c mmercially under the tradename VANLUBE® 7723 from R.T. Vanderbilt Company, Inc.

The dithiocarbamates of the formula III are known compounds. One of the processes of preparation is disclosed in U.S. Pat. No. 2,492,314. Groups R^4 and R^5 in the formula III represent branched and straight chain alkyl groups having 1 to 8 carbon atoms. Particularly preferred are antimony dithiocarbamates.

The phosphorodithioates of the formula IV are known, commercially available materials. One of the processes of preparation is taught by U.S. Pat. No. 4,215,067. Groups R^9 and R^{10} represent branched and straight chain alkyl groups having 1-22 groups and may be derived from fatty acids. The metal ion in formula III and IV may be sel cted from the following groups of the Periodic Table: IIA, IIIA, VA, VIA, IB, VIB and VIII. Amine salts of the compounds are also useful synergists of th invention. Exemplary, salts includ , among others, thos prepared from alkyl amin s and mixed alkyl amines. Particularly useful are fatty acid amines.

Th phosphorodithioate esters of the formula V are known compounds. One of th processes of manufactur is disclosed in U.S. Pat. No. 3,567,638. Groups R^4 and R^5 in the formula V may be the same or different and may be selected from branched and straight chain alkyl groups. Preferred are groups containing 1 to 8 carbon atoms.

The sulfur compounds are known to possess certain lubricating properties such as oxidation, wear and corrosion inhibiti n in various lubricating media. Sometimes, however, the sulfur comp unds alone do not provide adequat anti-wear protection for the varied heavy duty applications of many industrial and automotive lubricants.

Moreover, under certain conditions, the high concentrations of sulfur compounds may produce an adverse effect on the overall performance of the lubricant.

Unexpectedly, the above sulfur compounds produce synergistic antiwear effect when combined with organomolybdenum compounds in certain ratios. Synergism is displayed by compositions containing about 1 to 5 parts by weight of the sulfur compound to about 5 to 1 part by weight of the molybdenum compound.

Another advantage of the synergistic combination is that the compositions possess good antioxidant properties. Even in instances where the sulfur compounds do not possess an antioxidant activity, the combination with the molybdenum complexes provides a composition with good overall antioxidant properties.

The synergistic compositions may be incorporated in any lubricating media by known methods. The compositions impart antiwear as well as oxidation inhibiting and extreme pressure properties to natural and synthetic lubricants formulated as oils or greases.

The base oils employed as lubricant vehicles are typical natural and synthetic oils used in automotive and industrial applications such as, among others, turbine oils, hydraulic oils, gear oils, crankcase oils and diesel oils. Natural base oils include mineral oils, petroleum oil, paraffinic oils and the ecologically desirable vegetable oils. Typical synthetic oils include pentaerythritol esters, poly-alpha-olefins, hydrogenated mineral oils, silicones and silanes.

The compositions of the invention may be incorporated in the lubricant in an amount effective to produce the desired antiwear characteristics. An amount from about 0.1 to 10.0 percent will be sufficient for most applications. A preferred range is from about 0.5 to about 3.0 percent by weight of the total lubricant composition.

The lubricating compositions may contain other conventional additives depending on the intended use of the lubricant. For example, formulations may contain rust inhibitors such as metal salts of alkylnaphthalenesulfonic acids, demulsifiers, dispersants, detergents and supplemental antioxidants, particularly alkylated diphenylamines.

The grease formulations may contain various thickening agents such as, among others, silicate minerals, metal soaps and organic polymers.

The following examples are given for the purpose of illustrating the invention and are not intended in any way to limit the invention. All percentages and parts are based on weight unless otherwise indicated.

EXAMPLE 1

A laboratory test was conducted by using the original Falex machine to simulate the valve train wear of an automobile engine. The V-blocks and pin were washed in mineral spirits with an ultrasonic cleaner, rinsed with acetone, air dried and weighed. The test sample (60 g) was placed into the oil cup. The motor was switched on and the loading arm was placed on the ratchet wheel. Upon reaching the reference load of 227 kg, the ratchet wheel was disengaged and the load was maintained constant for 3.5 hours. Thereafter, the motor was switched off. The V-blocks and pin were washed, dried and weighed. The weight loss, a measure of wear, was recorded and compiled in Table I.

The test was performed with a molybdenum complex in conjunction with the following ashless sulfur compound synergists of the invention: S-dicarbobutoxyethyl 0,0-dipropylphosphorodithioate (hereinafter phosphorodithioate ester) and methylenebis(dibutyldithiocarbamate). The molybdenum complex was a reaction product of coconut oil, 2,2'-iminobisethanol and hexammonium salt of molybdic acid. The base oil was a hydrofinished naphthenic oil (ISO VG 22 manufactured by Sun Refining and Marketing Co.).

The results compiled in Table I indicate that the molybdenum complex and the above sulfur compounds act as synergists towards inhibition of wear.

Table I

Modified Falex Wear Test Component, Mass Percent						
Sample	1	2	3	4	5	6
Molybdenum complex	1.0	1.5	--	0.5	--	0.5
Phosphorodithioate ester	--	--	1.0	0.5	--	--
Methylenebis(dibutyldithiocarbamate)	--	--	--	--	1.5	1.0
Test Parameters						
Test Time, min.	40*	75*	20*	210	210	210
Total Weight Loss, mg.	433	542.8	--	14.6	86.4	3.4

*Test terminated due to excessive wear

EXAMPLE 2

The modified Falex Wear Test described in Example 1 was performed with the same molybdenum complex in conjunction with the following metal salts of the sulfur compound synergists: nickel dilauryldithiocarbamate, calcium di-2-ethylhexyldithiophosphate, aluminum di-2-ethylhexyldithiophosphate, tellurium di-2-ethylhexyldithiophosphate, and C_{12-14}-alkylamine salt of tert-octyl phosphates (hereinafter dithiophosphate amine salt). The base oil was a hydrofinished naphthenic oil (ISO VG 22).

The results compiled in Table II herein indicate that the molybdenum complex and the above salts of the sulfur compounds act as synergists towards inhibition of wear.

Table II

Modified Falex Wear Test Component, Mass Percent											
Sample	7	8	9	10	11	12	13	14	15	16	17
Molybdenum complex	1.5	--	0.5	--	0.5	--	0.5	--	0.5	--	0.5
Nickel dithiocarbamate	--	1.5	1.0	--	--	--	--	--	--	--	--
Calcium dithiophosphate	--	--	--	1.5	1.0	--	--	--	--	--	--
Aluminum dithiophosphate	--	--	--	--	--	1.5	1.0	--	--	--	--
Tellurium dithiophosphate	--	--	--	--	--	--	--	1.5	1.0	--	--
Dithiophosphate amine salts	--	--	--	--	--	--	--	--	--	1.5	1.0
Test Parameters											
Test Time, min.	75*	5*	210	5*	210	210	210	120*	210	2*	210
Total Weight Loss, mg.	542.8	366.8	14.9	366.6	90.1	33.5	18.4	84.8	17.7	5.6**	41.9

* Test terminated due to excessive wear

**High galling fail

EXAMPLE 3

A thin film oxygen uptake test was conducted essentially according to the method described by Chia-Soon Ju et al, J. Am. Soc. Lubricating Eng., 40, 2, 75-83, 1984. The oxidation induction time of the lubricant was measured under conditions which simulate the high temperature oxidation processes in automotive engines by modified rotary bomb oxidation test method ASTM D-2272. The test was conducted with 1.5 gram samples of hydrofinished naphthenic oil, ISO VG 22. The composition of the invention described in Example 1 and, for comparison, the individual components, were added to the oil in the amount indicated in Table III. The test was conducted at 160°C and initial oxygen pressure of 620.6 kPa (90 psi). A "pass" oil has a high induction time, while a "fail" oil has a low induction time. The compositions of the invention display good antioxidative effect as demonstrated by the data compiled in Table III.

Table III

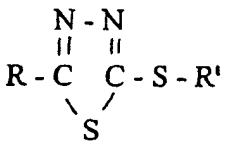
Thin Film Oxygen Uptake Test Component, Mass Percent				
Sample	18	19	20	21
Molybdenum complex	1.0	1.5	--	0.5
Methylenebis (dibutyldithiocarbamate)		--	1.5	1.0
Test Parameter				
Average Induction Time, min.	10	10	75	93

The above embodiments have shown various aspects of the present invention. Other variations will be evident to those skilled in the art and such modifications are intended to be within the scope of the invention as defined by the appended claims.

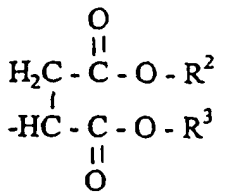
Claims

1. A synergistic antiwear composition consisting of

(a) an organomolybdenum complex prepared by reacting about 1 mole fatty oil, about 1.0 to 2.5 moles diethanolamine and a molybdenum source sufficient to yield about 0.1 to 12.0 percent of molybdenum based on the weight of the complex and (b) an organic sulfur compound selected from the group consisting of 1,3,4-thiadiazole compounds of the formula



wherein R and R' are independently selected from alkyl groups having 1 to 22 carbon atoms, terpene residue and maleic acid residue of the formula:

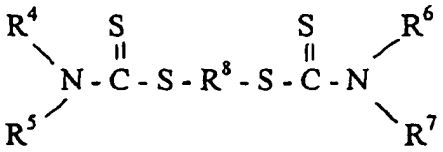


and R^2 and R^3 represent C_{1-22}-alkyl and C_{5-7}-cyloalkyl groups, and either R^2 or R^3 may be hydrogen, and either R or R' may be hydrogen when R^2 and R^3 are C_{9-22}-alkyl groups and the ratio of the molybdenum complex to the sulfur compound is about 1:5 to about 5:1.

2. A composition according to claim 1 wherein the 1,3,4-thiadiazole compound is 2,5-bispinanyl-1,3,4-thiadiazole.

3. A synergistic antiwear composition consisting of

(a) an organomolybdenum complex prepared by reacting about 1 mole fatty oil, about 1.0 to 2.5 moles diethanolamine and a molybdenum source sufficient to yield about 0.1 to 12.0 percent of molybdenum based on the weight of the complex and (b) a bisdithiocarbamate compound of the formula

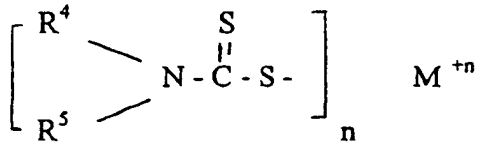


wherein R^4, R^5, R^6 and R^7 are aliphatic hydrocarbon groups having 1 to 13 carbon atoms and R^8 is an alkylene group having 1 to 8 carbon atoms, and the ratio of the molybdenum complex to the bisdithiocarbamate is about 1:5 to about 5:1.

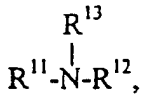
4. A composition according to claim 3 wherein the bisdithiocarbamate compound is methylenebis(dibutyldithiocarbamate).

5. A synergistic antiwear composition consisting of

(a) an organomolybdenum complex prepared by reacting about 1 mole fatty oil, about 1.0 to 2.5 moles diethanolamine and a molybdenum source sufficient to yield about 0.1 to 12.0 percent of molybdenum based on the weight of the complex and (b) a dithiocarbamate of the formula



wherein R^4 and R^5 represent alkyl groups having 1 to 8 carbon atoms and M represents metals of the periodic groups IIA, IIIA, VA, VIA, IB, VIB, VIII and a salt moiety formed from an amine of the formula

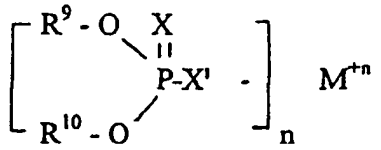


R^{11}, R^{12} and R^{13} being independently selected from hydrogen and aliphatic groups having 1 to 18 carbon atoms, and n is the valence of M, and the ratio of the molybdenum complex to the dithiocarbamate is about 1:5 to about 5:1.

6. A synergistic composition according to claim 5 wherein the dithiocarbamate is an antimony salt.

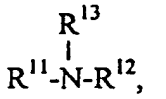
7. A synergistic antiwear composition consisting of

(a) an organomolybdenum complex prepared by reacting about 1 mole fatty oil, about 1.0 to 2.5 moles diethanolamine and a molybdenum source sufficient to yield about 0.1 to 12.0 percent of molybdenum based on the weight of the complex and
(b) a phosphorodithioate of the formula:



wh rein X and X' are ind pendently selected from S and O, R^9 and R^{10} represent hydrogen and alkyl gr ups having 1 to 22 carbon atoms, M represents metals of the periodic groups IIA, IIIA, VA, VIA, IB, VIB, VIII and a

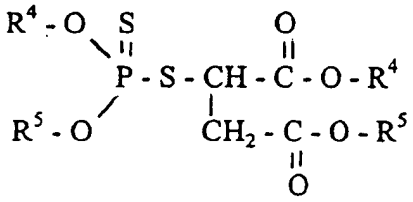
salt moiety formed from an amine of the formula



R^{11}, R^{12} and R^{13} being independently selected from hydrogen and aliphatic groups having 1 to 18 carbon atoms and n is the valence of M, and the ratio of the molybdenum complex to the phosphorodithioate is about 1:5 to about 5:1.

8. A synergistic antiwear composition consisting of

(a) an organomolybdenum complex prepared by reacting about 1 mole fatty oil, about 1.0 to 2.5 moles diethanolamine and a molybdenum source sufficient to yield about 0.1 to 12.0 percent of molybdenum based on the weight of the complex and
(b) a phosphorodithioate ester of the formula:



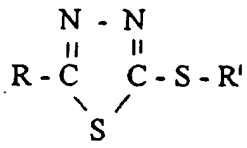
wherein R^4 and R^5 may be the same or different and are selected from alkyl groups having 1 to 8 carbon atoms, and the ratio of the molybdenum complex to the ester is about 1:5 to about 5:1.

9. A composition according to claim 8 wherein the ester is S-dicarbobutoxyethyl 0,0-dipropylphosphorodithioate.

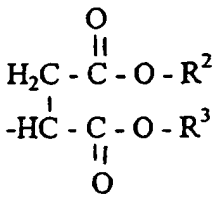
10. A lubricating composition comprising an oil of lubricating viscosity and about 0.1 to 10.0 percent by weight of a synergistic antiwear composition consisting of

(a) an organomolybdenum complex prepared by reacting about 1 mole fatty oil, about 1.0 to 2.5 moles diethanolamine and a molybdenum source sufficient to yield about 0.1 to 12.0 percent of molybdenum based on the weight of the complex and
(b) an organic sulfur compound selected from the group consisting of:

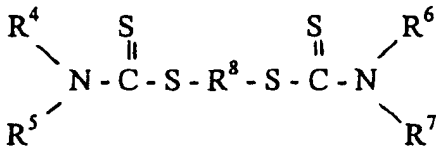
(i) 1,3,4-thiadiazole compounds of the formula



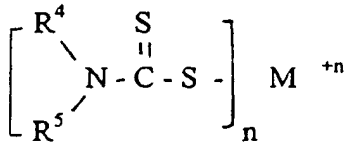
wherein R and R' are independently selected from alkyl groups having 1 to 22 carbon atoms, terpene residue and maleic acid residue of the formula



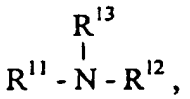
and R^2 and R^3 represent C_{1-22}-alkyl and C_{5-7}-cycloalkyl groups, either R^2 or R^3 may by hydrogen and either R or R' may be hydrogen when R^2 and R^3 are C_{9-22}-alkyl groups;
(ii) bisdithiocarbamate compounds of the formula:



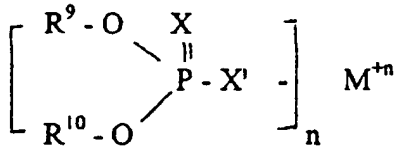
wherein R^4, R^5, R^6 and R^7 are aliphatic hydrocarbon groups having 1 to 13 carbon atoms and R^8 is an alkylene group having 1 to 8 carbon atoms;
(iii) dithiocarbamates of the formula:



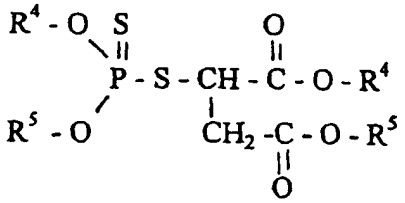
wherein R^4 and R^5 represent the groups defined hereinabove and M represents metals of the periodic groups IIA, IIIA, VA, VIA, IB, VIB, VIII and salt moiety formed from an amine of the formula



R^{11}, R^{12} and R^{13} being independently selected from hydrogen and aliphatic groups having 1 to 18 carbon atoms and n is the valence of M;
(iv) phosphorodithioates of the formula:



wherein X and X' are independently selected from S and O, R^9 and R^{10} represent hydrogen and alkyl groups having 1 to 22 carbon atoms, M represents metals and a salt moiety as defined above and n is the valence of M; and
(v) phosphorodithioat st rs of the formula:



wherein R^4 and R^5 may be the same or different and are selected from alkyl groups having 1 to 8 carbon atoms, and the ratio of the molybdenum complex to the sulfur compound is about 1:5 to about 5:1.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 10 6614

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X Y	WO 95 15368 A (EXXON RES&ENG CO.) * page 3, paragraph 3 - page 4 * * page 5, paragraph 5 - page 7, paragraph 1; table 1 *	5-7,10 1-4,8,9	C10M163/00 //(C10M163/00, 135:18,135:36, 137:10, 159:18), C10N10:12, C10N40:25
X Y	US 5 364 545 A (K.ARAI) * column 2, line 22 - column 4, line 3 * * column 8; table 1 *	5-7,10 1-4,8,9	
D,Y	US 4 880 437 A (T.J.KAROL) * column 1, line 21 - line 68 *	1,2	
D,Y	US 4 648 985 A (P.W.THORSELL) * column 2, line 35 - line 52 *	3,4	
D,Y	US 3 567 638 A (M.BRAID) * column 1, line 56 - line 72 *	8,9	
D,A	US 4 889 647 A (E.V.ROWAN) * the whole document *	1,10	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

C10M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	1 October 1997	Rotsaert, L

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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